# Early Sun, early Earth, early life ... early GISS

#### **Harold Urey**

From Wikipedia, the free encyclopedia

Harold Clayton Urey (April 29, 1893 – January 5, 1981) was an American physical chemist whose pioneering work on isotopes earned him the Nobel Prize in Chemistry in 1934 for the discovery of deuterium. He played a significant role in the development of the atom bomb, but may be most prominent for his contribution to theories on the development of organic life from non-living matter.<sup>[1]</sup>

Born in Walkerton, Indiana, Urey studied thermodynamics under Gilbert N. Lewis at the University of California. After he received his PhD in 1923, he was awarded a fellowship by the American-Scandinavian Foundation to study at the Niels Bohr Institute in Copenhagen. He was a research associate at Johns Hopkins University before becoming an associate professor of Chemistry at Columbia University. In 1931, he began work with the separation of isotopes that resulted in the discovery of deuterium.

During World War II Urey turned his knowledge of isotope separation to the problem of uranium enrichment. He headed the group located at Columbia University that developed isotope separation using gaseous diffusion. The method was successfully developed, becoming the sole method used in the early post-war period. After the war, Urey became professor of chemistry at the Institute for Nuclear Studies, and later Ryerson professor of chemistry at the University of Chicago.

Urey speculated that the early terrestrial atmosphere was probably composed of ammonia, methane, and hydrogen. One

Harold Clayton Urey



Harold Urey

Born	April 2	29, 1893

Walkerton, Indiana

Died January 5, 1981 (aged 87)

La Jolla, California

Nationality United States

Fields Physical chemistry

Institutions University of Copenhagen

Johns Hopkins University Columbia University Institute for Nuclear Studies University of Chicago

University of California, San Diego

Alma mater Earlham College

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University of California, Berkeley

Doctoral advisor Gilbert N. Lewis

Doctoral Stanley Miller students Harmon Craig

Known for discovery of deuterium

Miller-Urey experiment

heavy isotope should have lines redshifted by 1.1 to 1.8 ångströms  $(1.1 \times 10^{-10} \text{ to } 1.8 \times 10^{-10} \text{ metres})$ . Urey had access to a 21-foot (6.4 m) grating spectrograph, a sensitive device that had been recently installed at Columbia and was capable of resolving the Balmer series. It had a resolution of 1 Å per millimetre, so on this machine, the difference was about 1 millimetre. [17] However, since only one atom in 4,500 was heavy, the line on the spectrograph was very faint. Urey therefore decided to delay publishing their results until he had more conclusive evidence that it was heavy hydrogen. [16]

Urey and Murphy calculated from the Debye model that the heavy isotope would have a slightly higher boiling point than the light one. By carefully warming liquid hydrogen, 5 litres of liquid hydrogen could be distilled to 1 millilitre, which would be enriched in the heavy isotope by 100 to 200 times. To obtain five litres of liquid hydrogen, they traveled to the cryogenics laboratory at the National Bureau of Standards in Washington, D.C., where they obtained the help of Ferdinand Brickwedde, whom Urey had known at Johns Hopkins. [17]

The first sample that Brickwedde sent was evaporated at 20 K (~253.2 °C; ~423.7 °F) at a pressure of 1 standard atmosphere (100 kPa). To their surprise, this showed no evidence of enrichment. Brickwedde then prepared a second sample evaporated at 14 K (~259.1 °C; ~434.5 °F) at a pressure of 53 mmHg (7.1 kPa). On this sample, the Balmer lines for heavy hydrogen were seven times as intense. [16] The paper announcing the discovery of what we now call deuterium was jointly published by Urey, Murphy, and Brickwedde in 1932. [18] Urey was awarded the Nobel Prize in Chemistry in 1934 "for his discovery of heavy hydrogen". [19] He declined to attend the ceremony in Stockholm, so that he could be present at the birth of his daughter Mary Alice. [20]

Working with Edward W. Washburn from the Bureau of Standards, Urey subsequently discovered the reason for the anomalous sample. Brickwedde's hydrogen had been separated from water by electrolysis, resulting in depleted sample. Moreover, Francis William Aston now reported that his calculated value for the atomic weight of hydrogen was wrong, thereby invalidating Birge and Menzel's original reasoning. The discovery of deuterium stood, however.<sup>[16]</sup>

Urey and Washburn attempted to use electrolysis to create pure heavy water. Their technique was sound, but they were beaten to it in 1933 by Lewis, who had the resources of the University of California at his disposal. <sup>[21]</sup> Using the Born–Oppenheimer approximation, Urey and David Rittenberg calculated the properties of gases containing hydrogen and deuterium. They extended this to enriching compounds of carbon, nitrogen, and oxygen. These could be used as tracers in biochemistry, resulting in a whole new way of examining chemical reactions. <sup>[22]</sup> He founded the Journal of Chemical Physics in 1932, and was its first editor, serving in that capacity until 1940. <sup>[23]</sup>

Urey contributed a science article to *The Scientific Monthly* on Irving Langmuir, who invented atomic hydrogen welding in 1911 by utilizing 300 to 650 volts of electricity and tungsten filaments, and won the 1932 Nobel Prize in Chemistry for his work in surface chemistry.<sup>[24]</sup>

At Columbia, Urey chaired the University Federation for Democracy and Intellectual Freedom. He supported Atlanticist Clarence Streit's proposal for a federal union of the world's major democracies, and the republican cause during the Spanish Civil War. He was an early opponent of German Nazism and assisted refugee scientists, including Enrico Fermi, by helping them find work in the United States, and to adjust to life in a new country. [25]

#### Cesare Emiliani

From Wikipedia, the free encyclopedia

Cesare Emiliani (8 December 1922 – 20 July 1995) was an Italian-American scientist, geologist, micropaleontologist, and the founder of paleoceanography, developing the timescale of marine isotope stages, which despite modifications remains in very wide use today.

He established that the ice ages of the last half million years or so are a cyclic phenomenon, which gave strong support to the hypothesis of Milankovitch and revolutionized ideas about the history of the oceans and of the glaciations. He was also the proponent of Project "LOCO" (for Long Cores) to the U.S. National Science Foundation. The project was a success providing evidence of the history of the oceans and also serving to test the hypotheses of seafloor spreading and plate tectonics.

Cesare Emiliani was honored by having the genus *Emiliania* erected as home for the taxon *huxleyi*, which had previously been assigned to *Coccolithus*. He was further honored by receiving the Vega Medal of the Swedish Society for Anthropology and Geography (SSAG) (Swedish: Svenska Sällskapet för Antropologi och Geografi) in 1983, and the Alexander Agassiz Medal of the U.S. National Academy of

Cesare Emiliani in the early 1950s while conducting pioneering research at the University of Chicago. (Photo: Archives of the Rosenstiel School of Marine and Atmospheric Science, University of Miami)

Sciences in 1989 for his isotopic studies on Pleistocene and Holocene planktic foraminifera.

In his later years, he dedicated a great deal of time to promoting a calendar reform based on the Holocene calendar (HE) concept to eliminate the BC-AD chronology gap caused by the lack of a year 0.

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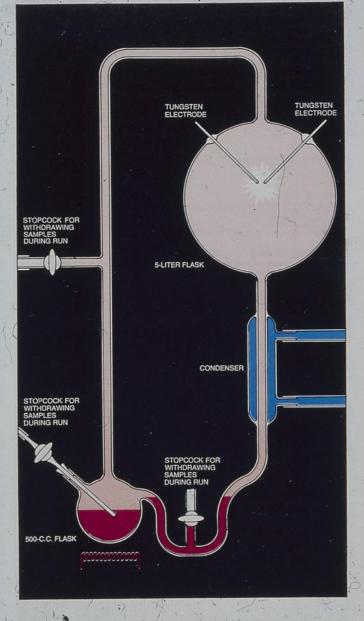
- 1 Biography
- 2 Popular works by Cesare Emiliani
- 3 Prominent works by Cesare Emiliani
- 4 See also
- 5 References

#### **Biography**

Cesare Emiliani was born in Bologna. His parents were Luigi and Maria (Manfredidi) Emiliani.



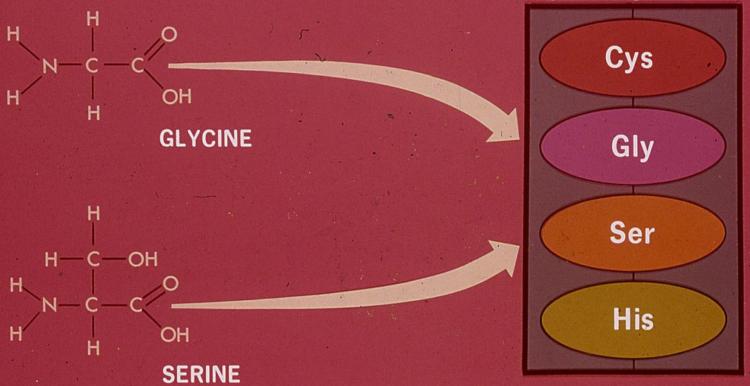
Stanley Miller



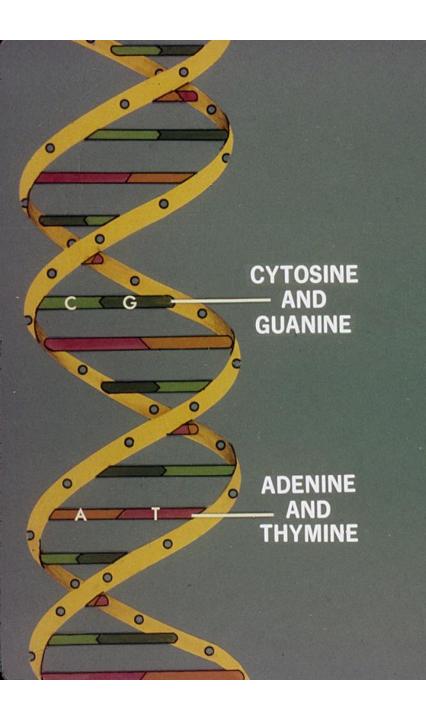
ORGANIC COMPOUNDS WERE SYNTHESIZED in an apparatus designed by Stanley L. Miller and Harold C. Urey at the University of Chicago to simulate conditions in the atmosphere of the primitive earth. Various mixtures of gases presumed to have been present in that atmosphere were admitted to the apparatus through the stopcock in the middle of the vertical tube at the left. Water in the 500-cubic-centimeter flask at the bottom of the tube was boiled to drive gases in a closed circuit through the apparatus. In the five-liter flask at the upper right the gases were subjected to a spark discharge (white) simulating energy inputs also presumed to have been present in the primitive atmosphere. The various compounds that were formed in the discharge (see top illustration on page 75) accumulated in solution at bottom of apparatus.

## SOME COMMON AMINO ACIDS

## PORTION OF INSULIN MOLECULE (A PROTEIN)



Scientists have begun to "crack" the genetic code by discovering how DNA signals the formation of a particular protein.



The nitrogen base pairs make up the rungs of the DNA molecule.

Solar Nebula

 $\bullet$   $O_2$   $O_3$ 

I.o.d.

#### The Role of Turbulent Convection in the Primitive Solar Nebula

#### I. Theory

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The theoretical framework for modeling the primordial solar nebula is presented in which convection is assumed to be the sole source of turbulence that causes the nebula to evolve. We use a new model of convective turbulence that takes into account the important effects of radiative dissipation, rotation, and anisotropy of convective motions. This model is based on a closure for the nonlinear interactions that employs the growth rates of hydrodynamic instabilities, a procedure that allows one to compute turbulence coefficients for instabilities other than convection. The vertical structure equations in the thin-disk approximation are developed for this new model, and a detailed comparison and critique of previous convective models of the solar nebula are presented. Numerical results are presented in a subsequent paper. © 1987 Academic Press, Inc.

#### I. INTRODUCTION

In recent years, it has become increasingly clear that the origin, structure, and evolution of planetary systems are but the last in a sequence of events that are thought i.e., one that removes the gas by causing it to begin with the collapse of a molecular cloud which fragments to form protostars surrounded by nebulae. The latter, due to rotation, assumes a disklike structure. Since the complete chain of events is clearly too complex to handle, one separates it into different parts in the hope that the real time sequence of events does not make this separation too unrealistic.

The "solar nebula" represents an intermediate phase in which the major period of infall from the collapsing cloud is over, but during which the gas and the grains forming the bulk of the nebula are still well mixed. The grains will ultimately drift toward midplane, where, upon becoming Jeans unstable, will give rise to the formation of proto-

planets. While some insight has been recently gained for the latter stage, the evolution of the solar nebula is far from being understood. The basic problem is that of finding a process to "clear" the nebula, to drift outward as well as inward toward the Sun. Since it is assumed that the solar nebula is not acted upon by external forces, one must search for an internally generated mechanism capable of initiating the drifting process. The problem is not an easy one, since the gas is locked in Keplerian orbits, which, if undisturbed, would remain so indefinitely.

To break the Keplerian motion, one may call upon the presence of large viscosities. Since, however, molecular forces are far too weak to produce the required effects, one usually resorts to "dynamical" processes to obtain an enhanced viscosity. This is where turbulence comes into play. It is known that if a fluctuating velocity is su-

#### The Role of Turbulent Convection in the Primitive Solar Nebula

#### II. Results

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Numerical results from a new model of the primordial solar nebula are presented in which convection is assumed to be the sole source of turbulence that causes the nebula to evolve. We introduce a new model of convective turbulence (described in detail in Paper I of this series) and new grain opacities computed from an improved physical model. The nebula is assumed to be in a stage prior to planetesimal formation in which gas and dust grains are mixed homogeneously, but in a stage after significant infall of matter from the outer cloud. Vertical structures for a thin nebular disk are calculated for different radii and accretion rates assuming vertical hydrostatic and thermal equilibrium; radial sequences of vertical solutions are constructed for constant accretion rates to represent quasistatic disk structures. Some aspects of our results differ markedly from those done previously by Lin and co-workers. Our values for the turbulent efficiency  $\alpha$  (10<sup>-2</sup> to 10<sup>-4</sup>) are much lower and much more sensitive to opacity and surface density. Our low values of  $\alpha$  result in (1) small turbulent speeds (≤1% of sound speed), which will alter prior computations of grain coagulation and sedimentation rates; (2) a more massive disk (>0.1Mo) that becomes gravitationally unstable at outer (super-Uranian) orbits; (3) a lower "best value" of the accretion rate (~1018.5 g sec-1); and (4) a longer characteristic dispersal time for the disk (>2 × 106 years), which may greatly exceed that inferred from young stellar objects. The high sensitivity of  $\alpha$  on surface density produces an inverse accretion rate-surface density relationship, which implies that the Lightman-Eardley diffusive instability develops throughout a steady disk structure in the radial direction, causing the disk, at least at the onset, to separate into rings. Because radial gradients are neglected in the base disk structure, the manner in which the instability evolves to finite amplitude is unknown, but it could prevent the disk from reaching a quasistatic structure altogether. We conclude that convection may not be the dominant source of turbulence needed to evolve young solar/stellar nebulae, and may in fact be a disruptive mechanism in disk structure. © 1987 Academic Press, Inc.

#### I. INTRODUCTION

The inner disklike region of the primordial solar nebula has been modeled and studied with respect to protoplanetary formation by Lin and co-workers (Lin and Papaloizou, 1980; Lin, 1981; Lin and Bodenheimer, 1982; referred to hereafter as LPB) using simplifying assumptions from thin accretion disk theory (cf. Pringle, 1981) and assuming that the disk is viscously cou-

pled by turbulence driven solely by thermal convection. LPB used a modified form of stellar mixing length theory (MLT) to estimate convective heat transport, mean speeds of convective motions, and turbulent (Reynolds) stresses. The nebular material was assumed to be a homogeneous mixture of gas and dust grains, with the latter providing virtually all of the material's opacity. LPB used grain opacity relations published by DeCampli and Cameron

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#### UV radiation from the young Sun and oxygen and ozone levels in the prebiological palaeoatmosphere

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UV measurements of young T-Tauri stars, resembling the Sun at an age of a few million years, have recently been made with the International Ultraviolet Explorer. They indicate that young stars emit up to 10<sup>4</sup> times more UV than the present Sun. The implications for the origin and evolution of O2 and O3 in the prebiological palaeoatmosphere are presented here. The results of photochemical calculations indicate that the O2 surface mixing ratio was a factor  $10^4$ – $10^6$ times greater than the standard value of  $10^{-15}$ . This new value reconciles the simultaneous existence of oxidized iron and reduced uranium.

A RELIABLE picture of the environment of the early Earth depends critically on the correct quantification of the amount of solar radiation impinging on the Earth. Standard stellar evolutionary models predict that 4,500 Myr ago, the Sun's luminosity was lower than today by ~30% (ref. 1). This has created the 'dim Sun paradox' because such dimming translates into a decrease of the Earth's effective temperature,  $T_{+}$ , of  $\sim$ 8%, sufficient to keep  $T_*$  below the freezing point of seawater for  $\sim 2,000$  Myr (ref. 2). On the other hand, there is evidence of liquid water as early as 3,500 Myr ago<sup>2</sup>, so a paradox arises. Explanations proposed to solve the problem include either increasing the greenhouse efficiency<sup>2-4</sup> or varying the Earth's early albedo5. In either case, one makes inferences about the physical parameters characterizing the palaeoatmosphere using astronomical data.

We consider here another astronomical input, the UV radiation from the Sun which had a great impact on the early atmosphere of the Earth<sup>6-12</sup>. In fact, UV radiation initiated the photochemical processes that led to the formation of oxygen (O<sub>2</sub>) and ozone (O<sub>3</sub>) in the prebiological palaeoatmosphere. By virtue of its strong absorption in the UV (200-300 nm), ozone protects life at the surface of the Earth from this lethal radiation. Hence, the evolution of ozone, and its variation over geological time had very important implications for the biological evolution of primitive organisms<sup>6-12</sup>. An accurate quantification of the levels of oxygen and ozone in the prebiological

		Table 1	Ratios of stellar to	r to solar UV line fluxes intercepted at the distance of the Earth				
λ(A)	Identity	T Tau	DR Tau	RW Aur	GW Ori	CoD-35°10525	RU Lup	S CrA
1,240	Νv	$2.5 \times 10^{5}$		$<4.0\times10^{3}$	2.3×10 <sup>5</sup>	$6.1 \times 10^4$	$2.4 \times 10^{3}$	
1,304	O i, S í	$1.3 \times 10^{5}$		$9.4 \times 10^{3}$	9.9×10 <sup>4</sup>	$3.0 \times 10^{4}$	$6.5 \times 10^{3}$	
1,335	Сп	$7.8 \times 10^{4}$		$9.6 \times 10^{2}$	$4.3 \times 10^{4}$	$1.7 \times 10^4$	$1.9 \times 10^{4}$	
1,400	Si tv	2.2×10 <sup>5</sup>	$5.5 \times 10^{4}$	1.2×10 <sup>4</sup>	2.3×10 <sup>5</sup>	$2.0 \times 10^4$	$3.3 \times 10^4$	$2.4 \times 10^{4}$
1,550	CIV	$1.4 \times 10^{5}$	$8.8 \times 10^{4}$	$3.2 \times 10^{3}$	1.5×10 <sup>5</sup>	2.9×10 <sup>4</sup>	1.2×10 <sup>4</sup>	$8.1 \times 10^{3}$
1,640	Не п	1.4×10 <sup>5</sup>	5.9×10 <sup>4</sup>	≤1.5×10 <sup>3</sup>	2.0×10 <sup>5</sup>	2.6×10 <sup>4</sup>	$5.8 \times 10^{3}$	≤7.7×10 <sup>3</sup>
1,813	Si 11, S 1	$2.9 \times 10^{4}$	$1.9 \times 10^{4}$		1.1×10 <sup>4</sup>	$2.8 \times 10^{3}$	$5.1 \times 10^{3}$	$5.6 \times 10^{3}$

The radii of the stars have been taken as (in solar radii): 6.8, 4.7, 3.1, 8.4, 3.4, 2.6, and 3.2, respectively

## The young Sun and the atmosphere and photochemistry of the early Earth

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The origin and evolution of the Earth's early atmosphere depend crucially on the dissipation time  $t_N$  of the primitive solar nebula, SN. Using different theories of turbulence, we estimate that for a 0.1  $M_{\odot}$  SN,  $t_N$  is 2.5–8.3 Myr. Because accretion times are usually much longer, we conclude that most planetary accretion must have occurred in a gas-free environment. Using new IUE data, a wavelength-dependent UV flux is constructed for the young Sun which is then used to study the photochemistry and concentrations of O, O<sub>2</sub>, O<sub>3</sub>, OH, H, HCO and formaldehyde  $H_2CO$  in the Earth's early prebiological atmosphere.

THERE is convincing observational evidence that the placental interstellar medium (ISM) from which the Solar System originated was a dense molecular cloud<sup>1,2</sup>. In fact, the recent evidence of the presence of short-lived nuclei in meteorites2 requires that the free-fall time scale for gravitational collapse  $(t_{\rm ff})$  be less than or comparable with the mean lifetime of  $^{26}$ Al  $(10^6 \text{ yr})$ , that is  $t_{\rm ff} \le 4 \times 10^7 / \sqrt{n_{\rm H}} < 10^6 \text{ yr}$ , which requires  $^2 n_{\rm H} > 10^6 \text{ yr}$ 10<sup>3</sup> cm<sup>-3</sup>, a value typical of molecular clouds. As molecular clouds are observed to be a major feature in our Galaxy, they constitute a reliable starting point for the processes that will eventually lead to the formation of stars and planetary systems<sup>3</sup>. A detailed analysis of the events that take place in such clouds. after an external agent has caused them to become unstable, has been worked out for a large variety of initial conditions<sup>4,5</sup>. Typically:  $M/M_{\odot} = 10^4$ ,  $\rho = 1.7 \times 10^{-23}$  g cm<sup>-3</sup>, T = 75 K,  $R = 6.6 \times 10^{19}$  cm,  $\Omega = 10^{-15}$  rad s<sup>-1</sup>, and  $J/M = 1.75 \times 10^{24}$  cm<sup>2</sup> s<sup>-1</sup>. Since T-Tauri stars have  $J/M = 10^{17} - 10^{18} \text{ cm}^2 \text{ s}^{-1}$ , a major effort has been dedicated to understand how to achieve a reduction of about 6 orders of magnitude in the value of J/M. The analysis indicates that the J/M reduction may be best achieved through a hierarchy of collapse and fragmentation and that the process yields binary fraagments, a reassuring result in view of the preponderance of binary star systems. The most relevant result of these computations is that the fragments form with masses larger than the local Jeans masses, ensuring their continuous collapse, thus placing, the hierarchical fragmentation model on firm foundations6.

Recent work<sup>6,7</sup> has, however, indicated difficulties with the previous scenario. Study of the collapse of a dark cloud (M = $50M_{\odot}$ , T = 10 K,  $R = 2 \times 10^{18}$  cm,  $\Omega = 3 \times 10^{-14}$  rad s<sup>-1</sup>,  $J/M = 10^{-14}$  $4 \times 10^{22}$  cm<sup>2</sup> s<sup>-1</sup>) indicates that a binary system is first formed with  $M/M_{\odot} = 8$ , each of the two fragment dividing further into a triple system with  $M/M_{\odot} = 2$ ,  $R = 2 \times 10^{15}$  cm, J/M =10<sup>20</sup> cm<sup>2</sup> s<sup>-1</sup>. The dynamics of each triple system indicates<sup>8</sup> that one object will be ejected in a time scale of  $t \approx 10^5$  yr, thus isolating one of the three partners which may then be considered a candidate for a massive primitive solar nebula as demanded in ref. 9. This sequence of events may, however, not be the true endpoint of the fragmentation process. A recent study of the fate of the  $2M_{\odot}$  ejected body indicates that it will further fragment into a multiple system, a process that will stop only at  $M < 0.1 M_{\odot}$ . These results show that fragmentation is not a self-regulating mechanism until one reaches  $M \sim 10^{-2} M_{\odot}$ , in agreement with an earlier analytic result<sup>10</sup> on opacity limited fragmentation. It has been suggested<sup>11</sup> that turbulence rather than simple fragmentation may be the relevant mechanism at work in star formation. If so, the resulting mass interval is  $5 \times 10^{-2} \le M/M_{\odot} \le 1$ , thus suggesting a solar nebula less massive than that of ref. 9 (see also ref. 12).

#### Protostellar evolution—UV spectrum

Observationally, the pre-main-sequence stars appear to pass through three phases of evolution. While extremely young, the protostars are detected primarily at IR wavelengths. This phase is thought to correspond with the accretion of the protostellar core, obscured beyond a shroud of dust. Theoretical models indicate that a  $1M_0$  star will remain in this early stage for  $10^5$  yr.

The second phase, characterized by the T-Tauri stars, begins as the protostars become visible. By this time, relatively small amount of gas and dust accompany the star; the stellar photosphere and bright chromosphere may be seen. The termination of this phase may be estimated from the maximum observed ages of the stars. Examinations of several associations, using member hot stars of known ages and stability arguments, indicate ages of 3-5 Myr (refs 14, 15). If the T-Tauri stage corresponds to the fully convective phase of pre-main-sequence evolution (vertical portion of the tracks of Fig. 1), then theoretical predictions may be used 16: 2 Myr for a  $2M_{\odot}$  star, 12 Myr for a  $1M_{\odot}$  star, and 40 Myr for a  $0.7M_{\odot}$  star. The ages for several T-Tauri stars in several young associations and clusters have been estimated from their HR diagram<sup>17</sup>. Figure 1 shows three evolutionary tracks, superimposed on data obtained for stars in Taurus-Auriga and Orion<sup>17</sup>, indicating ages from 10<sup>5</sup> to 10<sup>7</sup> yr. Considering that the stars are variable, rotate, possess magnetic fields and lose mass, complications with which the theory cannot yet deal completely, the overall agreement among ages derived by all these methods is good. Thus we conclude that, for a solar mass star, the T-Tauri stage of pre-mainsequence evolution begins when the star is ~105 yr old and lasts until it is  $\sim 6-12$  Myr old.

The phase following the T-Tauri stars, the radiative phase, although it comprises over 80% of the time required for the star to evolve to the main sequence, is not as well-defined observationally. Herbig<sup>18</sup> postulated the probable characteristics of the post T-Tauri star. Unexpectedly, a few such stars have been found through X-ray detection by the Einstein satellite <sup>19,20</sup>. The post T-Tauri stars exhibit the characteristics expected for protostars which are more evolved than the T-Tauri stars. However, no clear difference in ages has yet been established<sup>21</sup>. Thus clear examples of solar mass protostars with ages of 10–50 Myr are as yet lacking.

The Sun is a relatively normal star of moderate mass, temperature and luminosity; it is very reasonable to assume that it passed through these three phases of pre-main-sequence evolution. Therefore, we can use UV observations of pre-main-sequence stars to represent the UV spectrum of the youthful Sun. Several such stars have been observed with the International Ultraviolet Explorer (IUE)<sup>22-26</sup>. Virtually all of the data

Table 2	Stellar UV	flux as	a function of age
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Age (yr)	UV enhancement
10 <sup>6</sup>	104
10 <sup>7</sup>	500
$5 \times 10^7$	100
10 <sup>8</sup>	32
$5 \times 10^8$	8
10°	4
$5 \times 10^9$	1

			-	
	Table 4 Chemic	al reactions	39	Cl+
			40	ClO+O→
		Rate constant	41	ClO+NO→
	Donath an	3 -1 6 -1	42	Cl+CH <sub>4</sub> →H
łо.	Reaction	$(cm^3 s^{-1} or cm^6 s^{-1})$	43	Cl+H <sub>2</sub> →HCl+
	$O + O_2 + M \rightarrow O_3 + M$	$1.1 \times 10^{-34} \exp(510/T)$	44	Cl+HO <sub>2</sub> →HCl
1	$O + O_3 \rightarrow 2O_2$	$1.5 \times 10^{-11} \exp(-2.218/T)$	45	$Cl + H_2O_2 \rightarrow HCl$
2	$O(^1D) + O_2 \rightarrow O + O_2$	$3.2 \times 10^{-11} \exp(67/T)$	46	
4	$O(^1D) + O_2 \rightarrow O + O_2$ $O(^1D) + N_2 \rightarrow O + N_2$	$1.8 \times 10^{-11} \exp(107/T)$		Cl+HNO <sub>3</sub> →HCl
5	$N_2O + O(^1D) \rightarrow 2NO$	$6.6 \times 10^{-11}$	47	C1+CH <sub>2</sub> O→HC1+
5		$5.1 \times 10^{-11}$	48	HCl+OH→Cl+H <sub>2</sub>
7	$N_2O + O(^1D) \rightarrow N_2 + O_2$	$1.6 \times 10^{-32} \exp(584/T)$	49	$HCl+O \rightarrow Cl+OH$
7	$NO + O + M \rightarrow NO_2 + M$	$2.3 \times 10^{-12} \exp(-1,450/T)$	50	$C1+O_2+M \rightarrow C1O_2+$
8 9	$NO + O_3 \rightarrow NO_2 + O_2$	$9.3 \times 10^{-1} \exp(-1,430/T)$	51	CIO 114 CI 10
,	$NO_2 + O \rightarrow O_2 + NO$	9.3 × 10	51	$ClO_2 + M \rightarrow Cl + O_2 +$
0	$NO_2 + O_3 \rightarrow NO_3 + O_2$	$1.2 \times 10^{-13} \exp(-2,450/T)$	-52	C1+C1O <sub>2</sub> → 2C1O
	$NO + HO_2 \rightarrow NO_2 + OH$	$3.5 \times 10^{-12} \exp(250/T)$	53	$Cl + ClO_2 \rightarrow Cl_2 + O_2$
2	$NO_2 + OH + M \rightarrow HNO_3 + M$	*	54	$OH + OH + M \rightarrow H_2O$
3	$HNO_3 + OH \rightarrow NO_3 + H_2O$	$1.5 \times 10^{-14} \exp(650/T)$	55	$H_2O_2 + O \rightarrow OH + HO_2$
4	H <sub>2</sub> O+O(¹D) → 2OH	$2.2 \times 10^{-10}$	56	$OH + CH_4 \rightarrow CH_3 + H_2$
5	$H + O_2 + M \rightarrow HO_2 + M$	$2.1 \times 10^{-32} \exp(290/T)$	57	ClO+NO <sub>2</sub> +M→ClNO
6	$H + O_3 \rightarrow OH + O_2$	$1.4 \times 10^{-10} \exp(-470/T)$	58	O+CINO <sub>3</sub> →CIO+NO
7	$OH + O \rightarrow H + O_2$	$2.3 \times 10^{-11} \exp(110/T)$	59	$O(^{1}D) + HC1 \rightarrow OH + C$
8	$OH + O_3 \rightarrow HO_2 + O_2$	$1.6 \times 10^{-12} \exp(-940/T)$	60	$H_2 + OH \rightarrow H_2O + H$
9	OH+OH→H <sub>2</sub> O+O	$4.5 \times 10^{-12} \exp(-275/T)$	00	112 : 011 - 1120 : 11
)	$HO_2 + O \rightarrow OH + O_2$	4.0×10 <sup>-11</sup>	61	$CH_3 + O_2 + M \rightarrow CH_3O$
	•		62	$CH_3O_2 + HO_2 \rightarrow CH_3O_3$
1	$HO_2 + O_3 \rightarrow OH + 2O_2$	$1.1 \times 10^{-14} \exp(-580/T)$	63	CH <sub>3</sub> O <sub>2</sub> +NO→CH <sub>3</sub> O
2	$HO_2 + OH \rightarrow H_2O + O_2$	$4.0 \times 10^{-11}$	64	$CH_3O + O_2 \rightarrow CH_2O + 1$
3	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	$2.5 \times 10^{-12}$	65	CH <sub>2</sub> O+OH→HCO+
1	$H_2O_2 + OH \rightarrow HO_2 + H_2O$	$2.7 \times 10^{-12} \exp(-145/T)$	66	CH <sub>2</sub> O → OH + HCO + I
5	$OH + NO + M \rightarrow HNO_2 + M$	*	67	
5	$NO + NO_3 \rightarrow 2NO_2$	$2.0 \times 10^{-11}$		HCO+O <sub>2</sub> →CO+HO <sub>2</sub>
7	$O(^{1}D) + N_{2} + M \rightarrow N_{2}O + M$	$3.5 \times 10^{-37}$	68	CO+OH→H+CO <sub>2</sub>
8	$O(^{1}D) + H_{2} \rightarrow OH + H$	$9.9 \times 10^{-11}$	69	$CH_3Cl + OH \rightarrow Cl + produ$
9	$O(^{1}D) + CH_{4} \rightarrow OH + CH_{3}$	$1.4 \times 10^{-10}$	70	CH <sub>3</sub> OOH+OH→CH <sub>3</sub> O <sub>2</sub>
)	$NO_2 + O + M \rightarrow NO_3 + M$	$1.0 \times 10^{-31}$	71	OH+CH3CCl3→Cl+pro
١.	$NO_2 + NO_3 \rightarrow N_2O_5$	$1.5 \times 10^{-13} \exp(861/T)$	72	$O+O+M \rightarrow O_2+M$
2	$N_2O_5 \rightarrow NO_2 + NO_3$	$1.2 \times 10^{14} \exp(-10.319/T)$	73	$H+H+M\rightarrow H_2+M$
3	$N_2O_5 + H_2O \rightarrow 2HNO_3$	$1.0 \times 10^{-20}$	74	$H_2 + O \rightarrow OH + H$
4	$N_2O_5 + O \rightarrow 2NO_2 + O_2$	$3.0 \times 10^{-16}$	75	
5	$N + NO_2 \rightarrow N_2O + O$	$2.1 \times 10^{-11} \exp(-800/T)$		$H+HO_2 \rightarrow O_2+H_2$
6	$N + O_2 \rightarrow NO + O$	$4.4 \times 10^{-12} \exp(-3,220/T)$	76	$H+HO_2 \rightarrow H_2O+O$
37	$N+NO \rightarrow N_2+O$	3.4×10 <sup>-11</sup>	77	$H+HO_2 \rightarrow OH+OH$
8	$N + O_3 \rightarrow NO + O_2$	$1.0 \times 10^{-15}$		
			* See	ref. 34.

<sup>\*</sup> See ref. 34.

Table 2 Photochemical and chemical reactions

Reaction		Rate constant*
no.	Reaction	$(s^{-1}, cm^3 s^{-1} or cm^6 s^{-1})$
J1	$O_2 + h\nu \rightarrow O + O$	$4.7 \times 10^{-10}$ $6.3 \times 10^{-9}$
J2	$O_3 + h\nu \rightarrow O + O_2$	$2.2 \times 10^{-4}$ $8.5 \times 10^{-4}$
J3	$O_3 + h\nu \rightarrow O(^1D) + O_2$	$4.4 \times 10^{-3}$ $2.8 \times 10^{-2}$
J4	$H_2O + h\nu \rightarrow OH + H$	$1.1 \times 10^{-14}$ $5.1 \times 10^{-13}$
J5	$H_2O_2 + h\nu \rightarrow OH + OH$	$5.3 \times 10^{-5}$ $4.4 \times 10^{-4}$
J6	$H_2CO + h\nu \rightarrow H + HCO$	$4.8 \times 10^{-5}$ $1.6 \times 10^{-4}$
J7	$H_2CO + h\nu \rightarrow H_2 + CO$	$4.9 \times 10^{-5}$ $1.4 \times 10^{-4}$
18	$CO_2 + h\nu \rightarrow CO + O$	$1.3 \times 10^{-12}$ $6.3 \times 10^{-11}$
J9	$HCO + h\nu \rightarrow H + CO$	$1.3 \times 10^{-2}$ $5.8 \times 10^{-2}$
1	$O + O_2 + M \rightarrow O_3 + M$	$1.1 \times 10^{-34} \exp{(510/T)}$
2 3	$O + O_3 \rightarrow 2O_2$	$1.5 \times 10^{-11} \exp{(-2.218/T)}$
3	$O(^{1}D) + O_{2} \rightarrow O + O_{2}$	$3.2 \times 10^{-11} \exp{(67/T)}$
4	$O(^{1}D) + N_{2} \rightarrow O + N_{2}$	$2.0 \times 10^{-11} \exp{(107/T)}$
5	$H_2O + O(^1D) \rightarrow 2OH$	$2.3 \times 10^{-10}$
6	$H + O_2 + M \rightarrow HO_2 + M$	$2.1 \times 10^{-32} \exp{(290/T)}$
7	$H+O_3 \rightarrow OH+O_2$	$1.4 \times 10^{-10} \exp{(-470/T)}$
8	$OH + O \rightarrow H + O_2$	$4.0 \times 10^{-11}$
9	$OH + O_3 \rightarrow HO_2 + O_2$	$1.6 \times 10^{-12} \exp{(-940/T)}$
10	$OH + OH \rightarrow H_2O + O$	$1.0 \times 10^{-12} \exp{(-500/T)}$
11	$HO_2 + O \rightarrow OH + O_2$	$3.5 \times 10^{-11}$
12	$HO_2 + O_3 \rightarrow OH + 2O_2$	$1.1 \times 10^{-14} \exp(-580/T)$
13	$HO_2 + OH \rightarrow H_2O + O_2$	$4.0 \times 10^{-11}$
14	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	$2.5 \times 10^{-12}$
15	$H_2O_2 + OH \rightarrow HO_2 + H_2O$	$1.0 \times 10^{-11} \exp(-750/T)$
16	$O(^{1}D) + H_2 \rightarrow OH + H$	$9.9 \times 10^{-11}$
17	$OH + OH + M \rightarrow H_2O_2 + M$	†
18	$H_2O_2 + O \rightarrow OH + HO_2$	$2.8 \times 10^{-12} \exp(-2.125/T)$
19	$H_2 + OH \rightarrow H_2O + H$	$1.2 \times 10^{-11} \exp(-2,200/T)$
20	$H_2CO + OH \rightarrow HCO + H_2O$	$1.7 \times 10^{-11} \exp{(-100/T)}$
21	$H_2CO + O \rightarrow OH + HCO$	$2.8 \times 10^{-11} \exp(-1,540/T)$

```
5.0 \times 10^{-12}
22
         HCO + O_2 \rightarrow CO + HO_2
23
         CO+OH→H+CO<sub>2</sub>
                                                     \substack{2.8\times 10^{-34} \\ 8.3\times 10^{-33}} \exp{(710/T)}
24
         O+O+M \rightarrow O_2+M
25
         H+H+M\rightarrow H_2+M
                                                     3.0 \times 10^{-14} \exp(-4,480/T)

4.7 \times 10^{-11} (\times 0.29)
26
         H_2+O\rightarrow OH+H
27
         H+HO_2 \rightarrow O_2+H_2
                                                      4.7 \times 10^{-11} (\times 0.02)
         H+HO_2 \rightarrow H_2O+O
28
                                                     4.7 \times 10^{-11} (\times 0.62)
4.7 \times 10^{-11} (\times 0.69)
2.0 \times 10^{-33} \exp(-850/T)
3.0 \times 10^{-10}
29
         H+HO_2 \rightarrow OH+OH
         H+CO+M\rightarrow HCO+M
30
31
         H+HCO\rightarrow H_2+CO
         HCO+HCO\rightarrow H_2CO+CO 6.3×10<sup>-11</sup>
32
                                                     5.0 \times 10^{-11}
33
         OH+HCO→H<sub>2</sub>O+CO
                                                     1.0 \times 10^{-10}
         O+HCO+H+CO2
34
                                                     1.0 \times 10^{-10}
         O+HCO→OH+CO
35
                                                     1.0 \times 10^{-11}
         HO_2 + HCO \rightarrow H_2O_2 + CO
36
                                                     2.8 \times 10^{-11} \exp (-1,540/T)

1.0 \times 10^{-6} \text{ s}^{-1}
37
         H<sub>2</sub>CO+H→H<sub>2</sub>+HCO
         H<sub>2</sub>CO and H<sub>2</sub>O<sub>2</sub> rainout
```

<sup>\*</sup> Photolysis rates (s<sup>-1</sup>) for  $H_2 = 17$  p.p.m.v. are given for UV = 1 (first value) and UV = T-Tauri phase.

<sup>†</sup> See JPL Publ. 82-57 (1982).

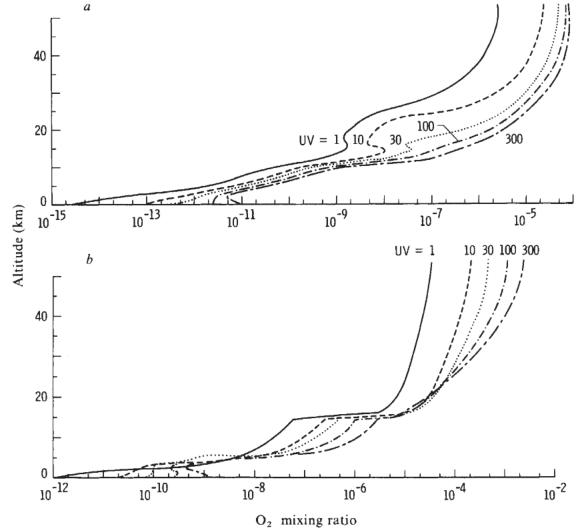


Fig. 1 Vertical distribution of O<sub>2</sub> in the prebiological palaeoatmosphere for levels of solar UV from 1 to 300 times the present value for a CO<sub>2</sub> level of: a, 280 p.p.m.v.; b, 28,000 p.p.m.v.

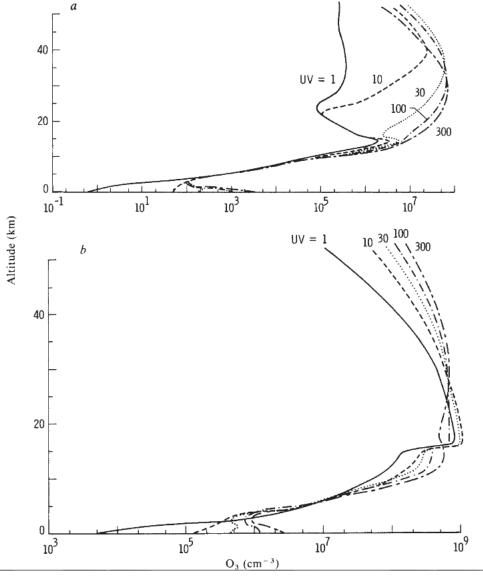


Fig. 2 Vertical distribution of O<sub>3</sub> in the prebiological palaeoatmosphere for levels of solar UV from 1 to 300 times the present value for a CO<sub>2</sub> level of: a, 280 p.p.m.v.; b, 28,000 p.p.m.v.

Table 5 Column density of O<sub>3</sub> in the prebiological palaeoatmosphere for various combinations of atmospheric CO<sub>2</sub> and solar UV flux

Solar UV flux	CO <sub>2</sub>	O <sub>3</sub> column (cm <sup>-2</sup> )
1*	1†	$1.72 \times 10^{12}$
	10	$2.49 \times 10^{14}$
	100	$1.38 \times 10^{15}$
10	1	$3.94 \times 10^{13}$
	10	$5.36 \times 10^{14}$
	100	$1.95 \times 10^{15}$
30	1	$1.50 \times 10^{14}$
	10	$7.81 \times 10^{14}$
	100	$2.06 \times 10^{15}$
100	1	$1.76 \times 10^{14}$
	10	$8.15 \times 10^{14}$
	100	$2.04 \times 10^{15}$
300	1	$1.52 \times 10^{12}$
	10	$9.41 \times 10^{14}$
	100	$2.19 \times 10^{15}$

#### THE HISTORY OF THE EARTH AND THE FOSSIL GROWTH RHYTHMS

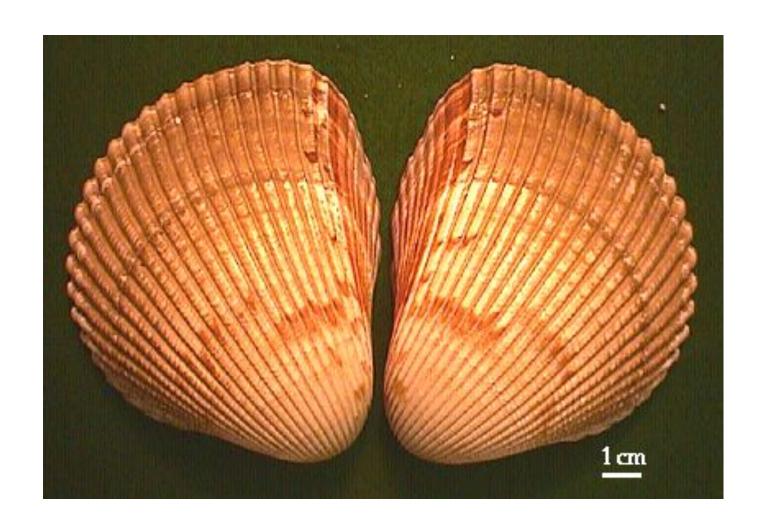
V. Canuto\*

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#### Model

- Kepler's Law, conservation of angular momentum
   Data
- N= # of Solar days in a year
- S= # of Solar days in a Synodic monthOutput
- I.o.d.
- Earth's spin
- Earth-Moon distance
- Earth's moment of inertia
- Earth's energy loss



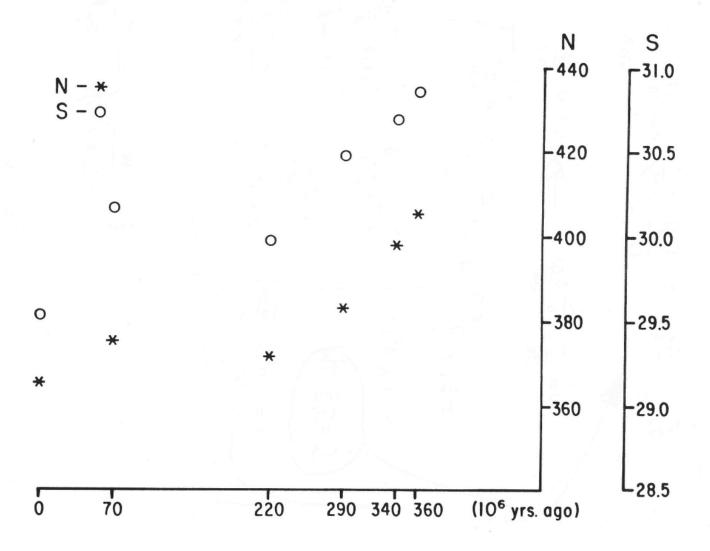
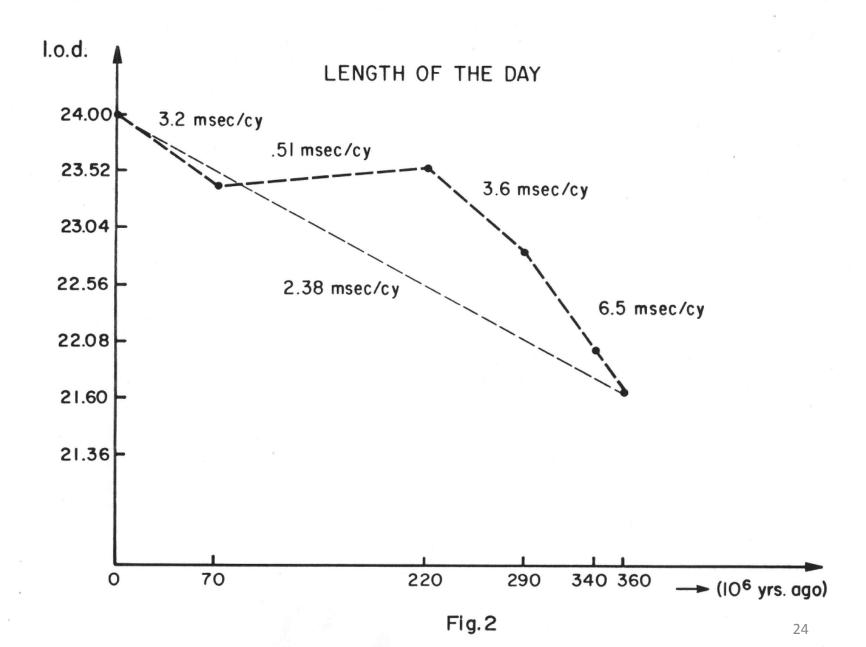
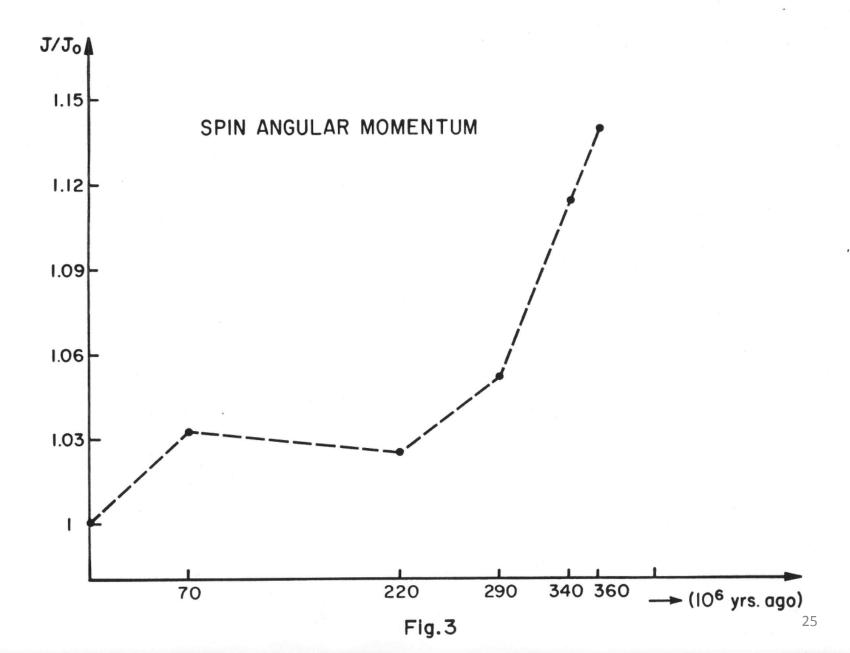
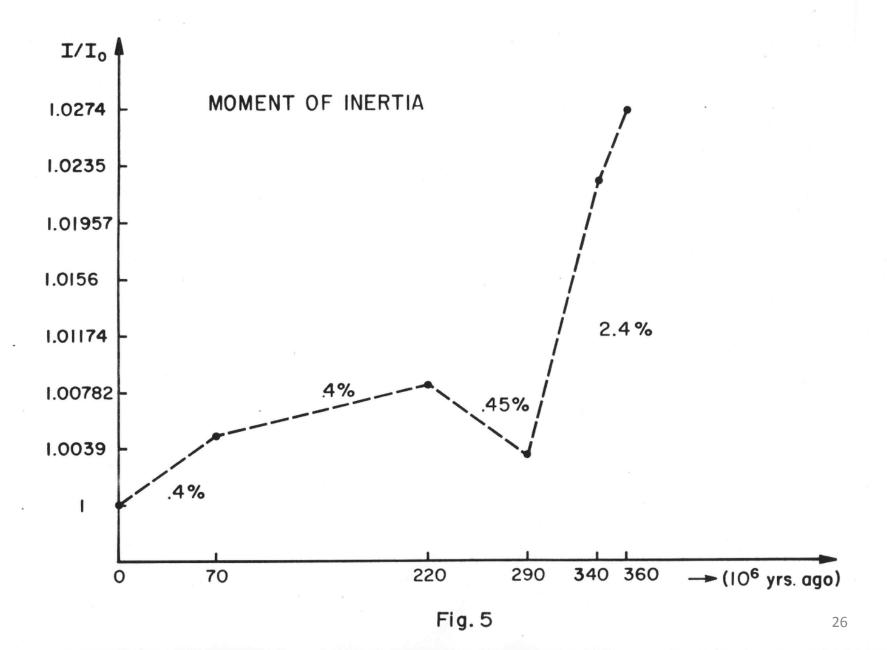


Fig.I



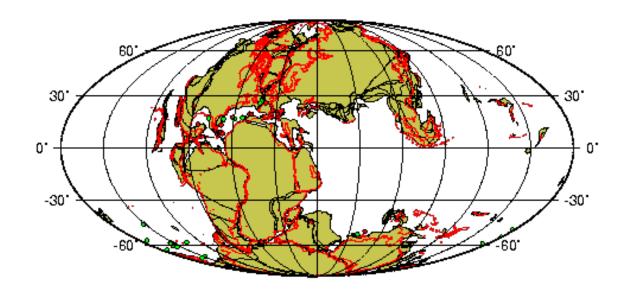




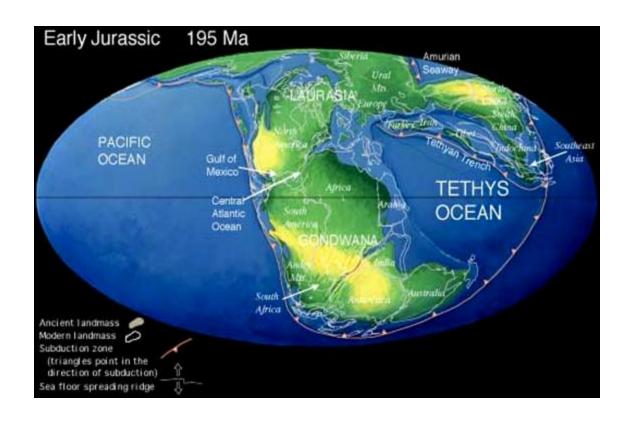
The basic premise is that 180 million to 200 million years ago, the entire land mass of the Earth was in fact connected. This connected land mass is known as Pangea and is thought to have looked like this:

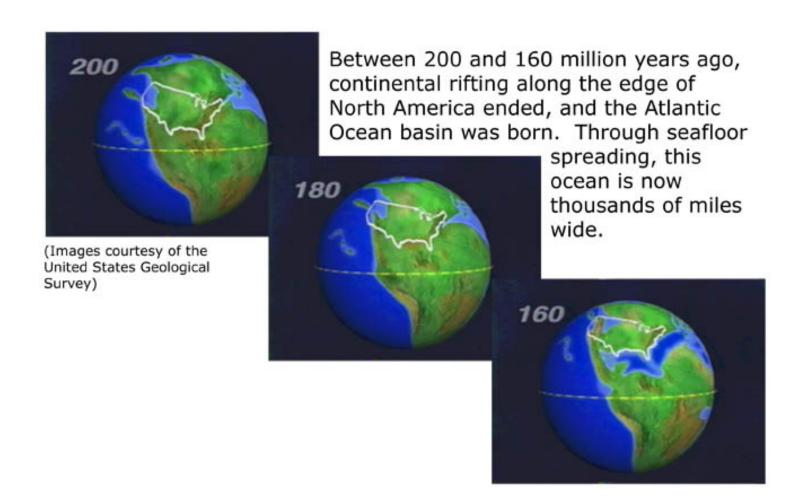


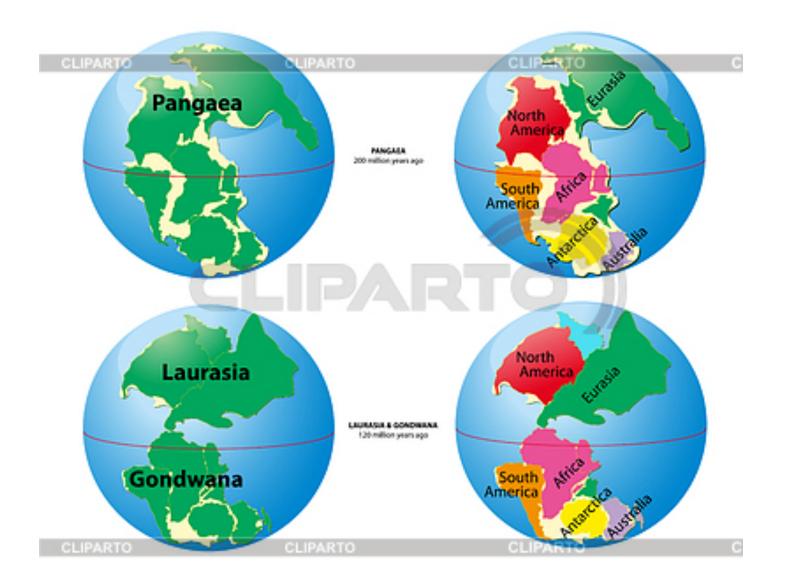
### Over time the plates drifted apart and individual continents gained their identity.

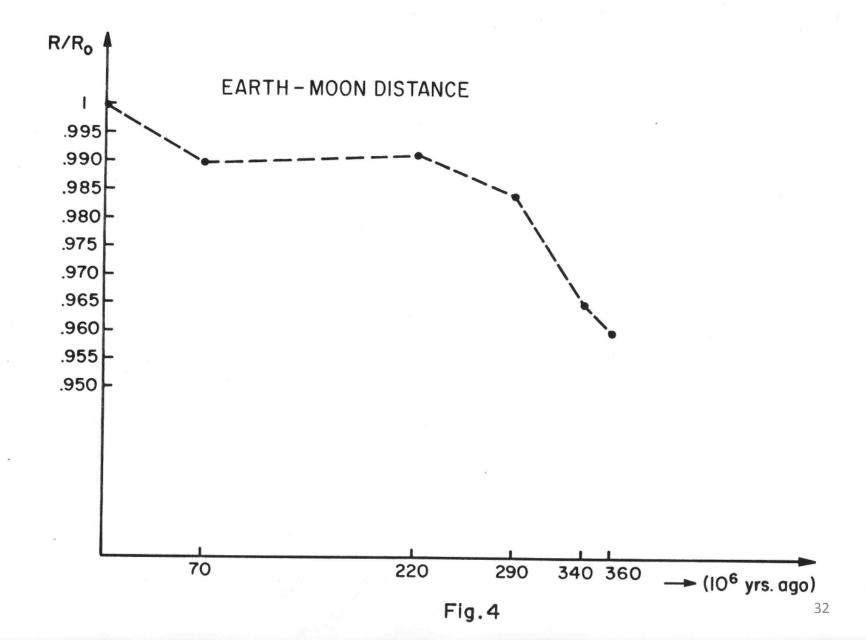


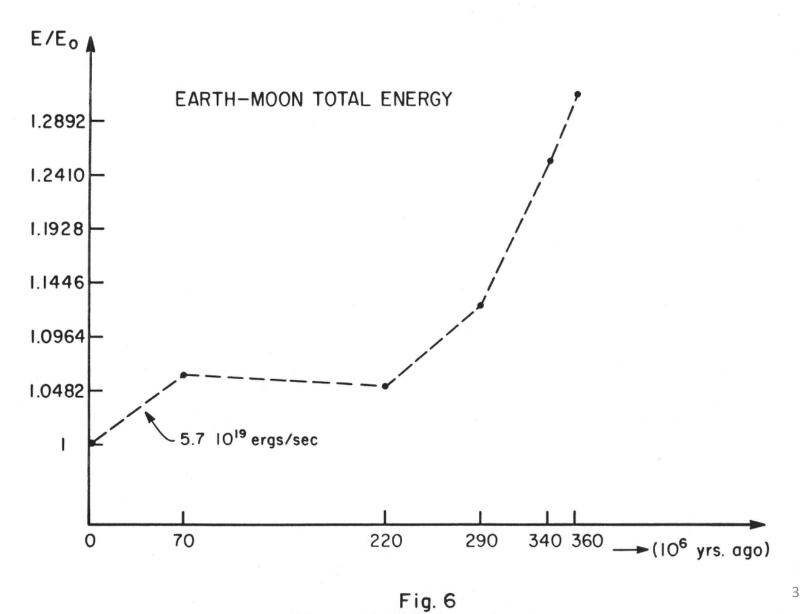
150 My Reconstruction











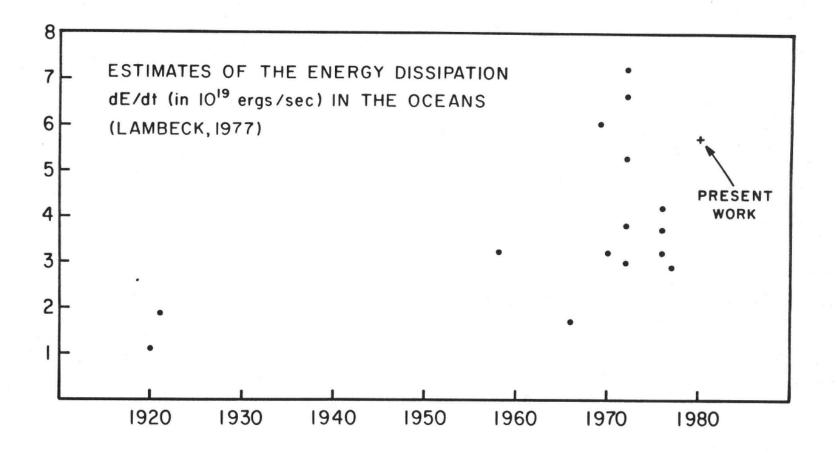


Fig.7



Deep-Sea Research 1 45 (1998) 1977-2010

## Abyssal recipes II: energetics of tidal and wind mixing

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#### Abstract

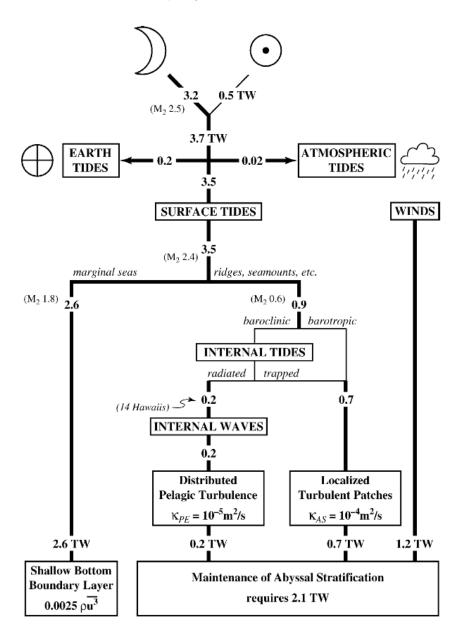
Without deep mixing, the ocean would turn, within a few thousand years, into a stagnant pool of cold salty water with equilibrium maintained locally by near-surface mixing and with very weak convectively driven surface-intensified circulation. (This result follows from Sandström's theorem for a fluid heated and cooled at the surface.) In this context we revisit the 1966 "Abyssal Recipes", which called for a diapyenal diffusivity of  $10^{-4}$  m²/s (1 egs) to maintain the abyssal stratification against global upwelling associated with 25 Sverdrups of deep water formation. Subsequent microstructure measurements gave a pelagic diffusivity (away from topography) of  $10^{-5}$  m²/s — a low value confirmed by dye release experiments.

A new solution (without restriction to constant coefficients) leads to approximately the same values of global upwelling and diffusivity, but we reinterpret the computed diffusivity as a surrogate for a small number of concentrated sources of buoyancy flux (regions of intense mixing) from which the water masses (but not the turbulence) are exported into the ocean interior. Using the Levitus climatology we find that 2.1 TW (terawatts) are required to maintain the global abyssal density distribution against 30 Sverdrups of deep water formation.

The winds and tides are the only possible source of mechanical energy to drive the interior mixing. Tidal dissipation is known from astronomy to equal 3.7 TW (2.50  $\pm$  0.05 TW from  $M_2$  alone), but nearly all of this has traditionally been allocated to dissipation in the turbulent bottom boundary layers of marginal seas. However, two recent TOPEX/POSEIDON altimetric estimates combined with dynamical models suggest that 0.6–0.9 TW may be available for abyssal mixing. A recent estimate of wind-driving suggests 1 TW of additional mixing power. All values are very uncertain.

A surprising conclusion is that the equator-to-pole heat flux of 2000 TW associated with the meridional overturning circulation would not exist without the comparatively minute mechanical mixing sources. Coupled with the findings that mixing occurs at a few dominant sites, there

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## **Summary: from Bivalve to the MOC**

- Kepler's third law
- Angular Momentum Conservation
- Bivalve
- $K_{\rho} = \Gamma \frac{\varepsilon}{N^2} \implies O(1 \text{cm}^2 \text{s}^{-1}) = 1 \text{Munk}$
- Oceanic diapycnal diffusivity
- MOC

